

SUPPORTED RHODIUM-PHOSPHINE HYDROGENATION CATALYSTS OF HIGH MOBILITY AND REACTIVITY

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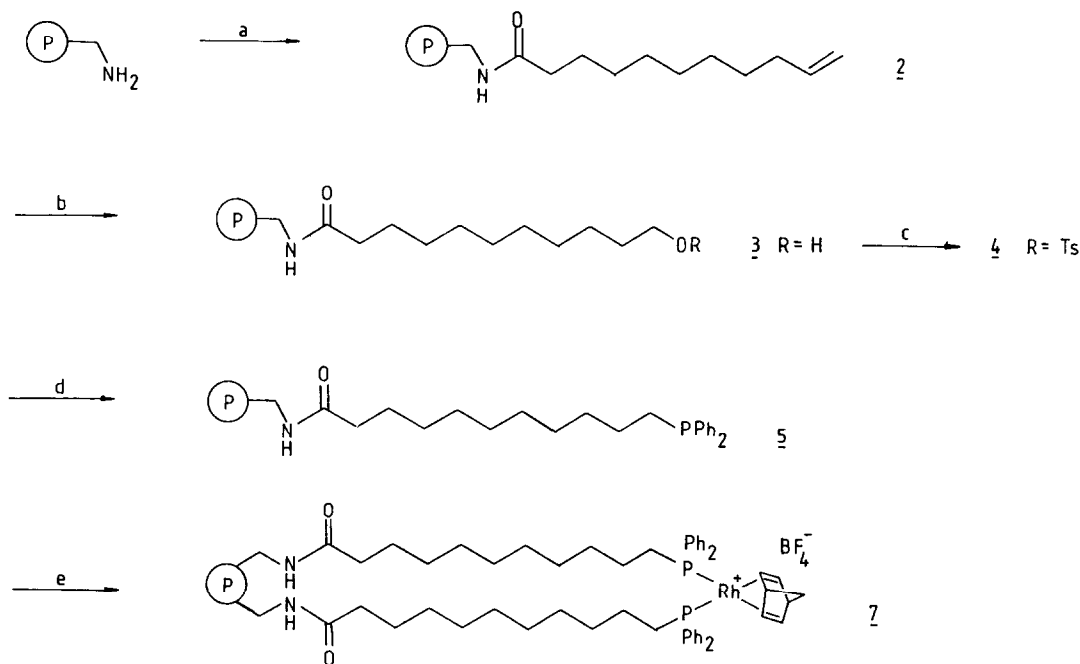
Abstract Cationic rhodium complexes derived from a polystyrene-bonded long-chain alkyldiphenylphosphine are effective hydrogenation catalysts.

Homogeneous hydrogenation of olefins by both neutral¹ and cationic² rhodium phosphine complexes may be rapid, efficient and selective, but suffers from disadvantages when it is desired to recover and recycle the catalyst. Many attempts have been made to combine their advantages with those of heterogeneous catalysts by employing polymer analogues designed to have an active site structure similar to the soluble species³. These have most commonly involved the synthesis of diphenylphosphino- and diphenylphosphinomethyl polystyrenes, cross-linked to varying degrees, from which the catalytically active species is generated *in situ* by reaction with an appropriate rhodium (I) complex⁴. Analogous silica-supported catalysts have been reported more recently⁵. The applicability of supported hydrogenation catalysts has been rather limited and their performance disappointing. This is due to two factors. With highly substituted cross-linked polystyrenes, diffusion of substrate into the polymer lattice is slow, thus lowering the overall rate of hydrogenation. This is not the case with highly-substituted polystyrenes, or silica-supported catalysts, but here the effective molecular weight of the active species is much higher (> 5000). In either case it is necessary to use a much higher weight of supported catalyst to achieve a given reaction rate.

We report here the synthesis of catalysts which lack this drawback and preliminary aspects of their application to hydrogenation. A basic difference is that the diphenylphosphine residue is spaced from the polymer backbone by a long alkyl chain, which exerts a profound effect on catalyst properties. The advantages of this approach have previously been demonstrated.^{6,7} For example, O-alkylation of sodium 2-naphthoxide in water is much more effectively catalysed by polystyrenes bearing a $(\text{CH}_2)_{10}^+ \text{NMe}_2$ side-chain than by simple ion-exchange resins⁶. It is thought that the inherent flexibility of the alkyl chain allows micelle-like aggregation of quaternary-ammonium groups at the polymer-water phase boundary.

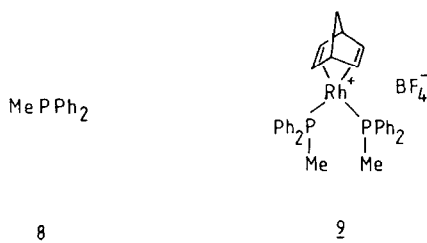
Preparation of polymeric phosphines is conducted according to the Scheme. Aminomethylpolystyrene (2% cross-linked, > 94% substituted) reacts with acid-chloride **1** giving amide **2** which is converted by BH_3 ; THF into the primary alcohol **3**. Further reaction of **3** with an excess of *p*-toluenesulphonyl chloride in pyridine gives the polymeric tosylate **4** which is stored at 0° . All polymers in the sequence gave satisfactory C, H, N, (S) analyses, and c.m.r. data are in accord with the proposed structures.

Tosylate 4 reacts with a 5-molar excess of Ph_2PLi in THF (20 mins at 0° , 1h. at RT) giving the desired polymeric phosphine 5 (4.98% P, effective MW = 615) with 69% substitution of available sites.



Scheme a) $\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{COCl}$ [1], pyridine, 60° , 12h., b) $\text{BH}_3\cdot\text{SMe}_2$, 0° , 1h., then H_2O_2
 c) p TsCl , pyridine, 0° , 20 h., d) Ph_2P , Li, THF, 3h. e) [6], acetone, 30 mins.

The phosphorus -31 n.m.r. spectrum of 5 in CH_2Cl_2 shows only a single adsorption ($\delta = -21$ p.p.m, $\omega_{1/2} = 80$ Hz). Addition of an equimolar quantity of bis-norbornadiene rhodium (I) tetrafluoroborate 6 and thorough mixing followed by standing at ambient temperature gives a new spectrum (δ 15 p.p.m, $\omega_{1/2} = 400$ Hz) consistent with the formation of 7 [c.f. 8, -26 p.p.m, 9, 3.5 p.p.m.]⁸. Addition of a molar deficiency of the cationic complex 6 (20 mgs.) to polymeric phosphine 5 (200 mgs.) swollen in CH_2Cl_2 shows initially a sharp line at -21 p.p.m. and a very broad line at -2 p.p.m. ($\omega_{1/2} \sim 1000$ Hz). On standing for 2 hours at ambient temperature the only signal is a broad singlet at -9 p.p.m. We interpret these observations to suggest that macroscopic diffusion equilibrating bound and free phosphines is slow, but that site-exchange between 7 and 5 is rapid on the n.m.r. time-scale implying considerable fluidity in the polymer. This contrasts with the much longer time-scale of exchange processes in conventional supported catalysts⁹.



Application of 7 to the hydrogenation of oct-1-ene in acetone is recorded in the FIGURE. The catalyst was prepared by adding a pre-weighed quantity of 5 (usually 50 mg.) to 6 in acetone solution (normally 12 mg. in 5 ml.). After stirring for 30 minutes under argon, hydrogen was admitted and stirring continued for a further 15 minutes. Oct-1-ene (300 μL) was then injected and the rate of hydrogen uptake recorded. It will be seen (a) that the rate of hydrogenation is comparable, or superior to that observed with homogeneous catalysts under comparable conditions and (b) that the presence of excess phosphines is detrimental, again implying a high degree of fluidity. The supported catalyst normally remains light-orange throughout the cycle but if excess 6 is employed, or HClO_4 added then the presence of rhodium metal is apparent during hydrogenation. The fall-off in rate as reaction proceeds is due to isomerisation (oct-2-ene observed by n.m.r.) and this appears to be a more serious side-reaction with 9 than with 7. Further studies will elucidate the relative reactivity of different olefins and the efficiency of related asymmetric phosphines.

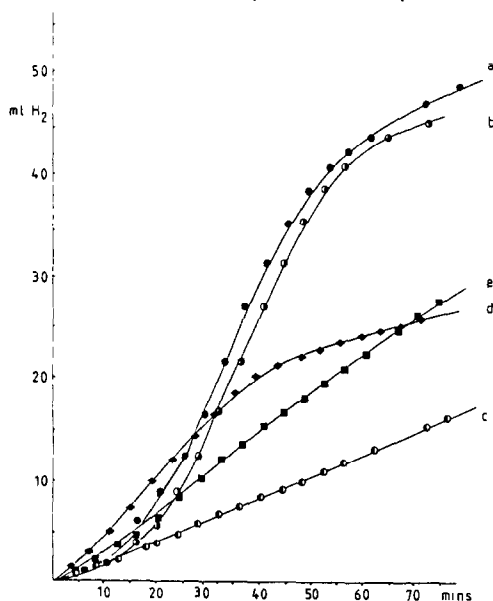


FIGURE Hydrogenation of 1-octene at atmospheric pressure, acetone solution.

- a) 5 : 6, Rh:P = 1:2.25, [Rh] = 32 μmoles
15 minutes prehydrogenation.
- b) As a) separate batch of polymer
- c) 5 : 6, Rh:P = 1:2.6 [Rh] = 28 μmoles
15 minutes prehydrogenation.
- d) 9 prepared in situ, [Rh] = 32 μmoles
15 minutes prehydrogenation.
- e) $\text{ClRh}(\text{PPh}_3)_3$, [Rh] = 21 μmoles

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